

Evaluation, prediction, and protection of water quality in Danjiangkou Reservoir, China

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Abstract

The water quality in the Danjiangkou Reservoir has attracted considerable attention from the Chinese public and government since the announcement of the Middle Route of the South to North Water Diversion Project (SNWDP), which commenced transferring water in 2014. Integrated research on the evaluation, prediction, and protection of water quality in the Danjiangkou Reservoir was carried out in this study in order to improve environmental management. Based on 120 water samples, wherein 17 water quality indices were measured at 20 monitoring sites, a single factor evaluation method was used to evaluate the current status of water quality. The results show that the main indices influencing the water quality in the Danjiangkou Reservoir are total phosphorus (TP), permanganate index (COD_{Mn}), dissolved oxygen (DO), and five-day biochemical oxygen demand (BOD₅), and the concentrations of TP, BOD₅, ammonia nitrogen (NH₃-N), COD_{Mn}, DO, and anionic surfactant (Surfa) do not reach the specified standard levels in the tributaries. Seasonal Mann–Kendall tests indicated that the COD_{Mn} concentration shows a highly significant increasing trend, and the TP concentration shows a significant increasing trend in the Danjiangkou Reservoir. The distribution of the main water quality indices in the Danjiangkou Reservoir was predicted using a two-dimensional water quality numerical model, and showed that the sphere of influence from the tributaries can spread across half of the Han Reservoir if the pollutants are not controlled. Cluster analysis (CA) results suggest that the Shending River is heavily polluted, that the Jianghe, Sihe, and Jianhe rivers are moderately polluted, and that they should be the focus of environmental remediation.

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Keywords: Water quality; Single factor evaluation method; Mann–Kendall test; Numerical modeling; Cluster analysis; Dangjiangkou Reservoir

1. Introduction

Water quality tends to degenerate gradually with human interventions, such as hydrological alterations (Booker and Woods, 2014), land use change (Seeboonruang, 2012), inputs of toxic chemicals and nutrients (Gevrey et al., 2010), and changes in other physicochemical properties of water (Paul

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and Meyer, 2001; Vanlandeghem et al., 2012), which cause a series of environmental problems, for example, shortage of drinking water (Bao et al., 2012), deterioration of aquatic ecological systems (Hu and Cheng, 2013), and emergence of endemic diseases (Zhao et al., 2012). With environmental pollution becoming an increasingly serious problem, the issue of water quality has attracted serious attention from the public and the government. The primary concern of the public is the current status of water quality, so water quality evaluation has been extensively studied (Nives, 1999; Simeonov et al., 2003; Crosa et al., 2006; Olsen et al., 2012). However, governments are not only concerned about the current status, but also about the future trends (Crosa et al., 2006; Chang, 2008) as well as

measures for the protection of water quality (Zhu et al., 2011). Therefore, integrated research on water quality evaluation, prediction, and protection is one of the most important research issues.

Different water quality evaluation methods have been developed. In the past, single factor evaluation methods were widely used in rivers (Xu et al., 2012), reservoirs, and lakes (Xu, 2005). Comprehensive index methods, such as the water quality index method, were developed by the National Sanitation Foundation (NSF) (Ott, 1978), and several modified water quality indices have been developed based on this method (Nasiri et al., 2007). Some researchers then switched to the water quality evolution trend analysis, for which many methods have been successfully used, such as the rank correlation method (El-Shaarawi et al., 1983), time series analysis method (Long et al., 2009), and parametric test method (Kundzewicz and Robson, 2004; Yenilmez et al., 2011), but there are still no good solutions to seasonal and missing-value effect problems, and these trend analysis methods cannot show the distribution of water quality indices in water bodies.

The Danjiangkou Reservoir is the water source for the Middle Route of the South to North Water Diversion Project (SNWDP), and the success of the SNWDP depends on the water quality in the Danjiangkou Reservoir. Therefore, protection of water quality in the Danjiangkou Reservoir is of extreme importance. Generally, water quality management in reservoirs and lakes is more complicated than in rivers, since the water in reservoirs and lakes resides for a long time, and sedimentation and transformations can occur. After the Danjiangkou Reservoir was selected as the water source for the middle route of the SNWDP, the water quality goal was determined to be Grade II according to the *Chinese Environmental Quality Standards for Surface Water* (GB 3838-2002). This is quite a strict requirement. As a result, many sources of point source pollution around the reservoir have been removed by the government and many environmental remediation

projects have been carried out in recent years. So far, the good water quality of the reservoir has been well maintained, and almost all the indices satisfy the requirements. However, water quality in some tributaries is still below the required standard, which is a potential threat to the water quality in the Danjiangkou Reservoir.

Little attention has been paid to evaluation, prediction, and protection of the water quality in the Danjiangkou Reservoir. Therefore, this study focused on the water quality in the Danjiangkou Reservoir, analyzed the current status of water quality with a single factor evaluation method (the recommended method for environmental protection standards in China), and investigated the evolution trend of water quality with the seasonal Mann–Kendall method, which can deal well with seasonal and missing-value effect problems. Then, the distributions of water quality indices were simulated with a two-dimensional numerical model, which can identify the pollution areas conveniently. Based on these analyses, a hierarchical clustering method was used to classify the tributaries in order to identify the main pollution source. Finally, proper protection measurements are proposed for the polluted tributaries for better water quality management of the Danjiangkou Reservoir. All the analysis results can effectively support water quality protection management for the government.

2. Study area

The Danjiangkou Reservoir is located in the upper reaches of the Hanjiang River (Fig. 1), the largest tributary in the middle reaches of the Yangtze River, and the water source of the SNWDP, which sends water to Beijing and other northern cities in China. It has a surface area of 1 050 km², and a total storage capacity of 29.05 km³ when the water reaches its normal level of 170 m. The reservoir catchment area is 95 200 km², and the average annual inflow is about 38.80 km³.

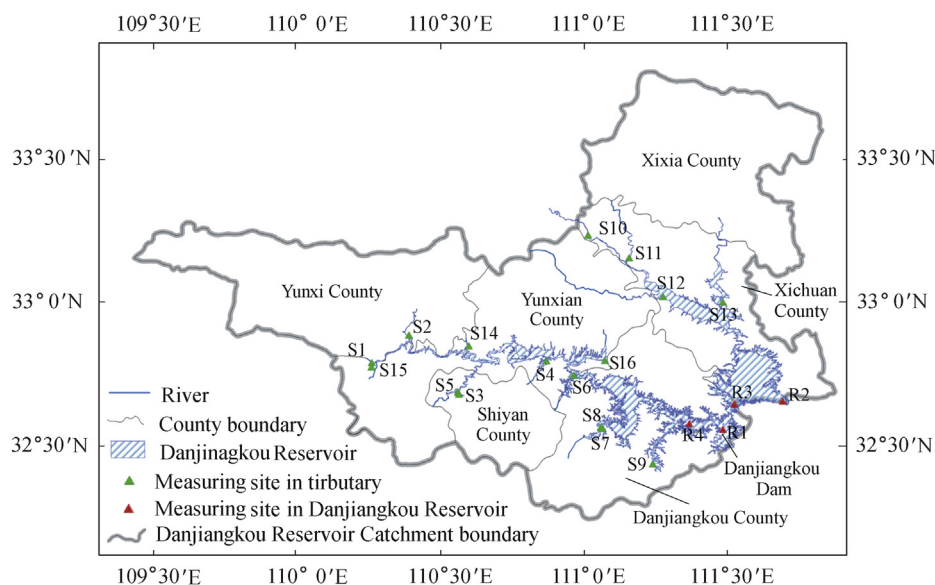


Fig. 1. Locations of Danjiangkou Reservoir and monitoring sites.

The average annual precipitation is 833 mm, and 75% of the annual precipitation falls in May to October. The Danjiangkou Dam is located at the junction of the Hanjiang River and Danjiang River, so the Danjiangkou Reservoir can be subdivided into the Han Reservoir and Dan Reservoir. There are six counties in the reservoir catchment: Xixia, Xichuan, Yunxi, Yunxian, Danjiangkou, Shiyan counties, with a combined population of 3.14 million (Fig. 1). The gate for the water diversion canal is located at Taocha. There are approximately 200 tributaries in the Danjiangkou Reservoir Catchment, of which 16 main tributaries make up 90% of the whole drainage area. Information for these 16 tributaries is described in Table 1.

3. Materials and methods

3.1. Sample data collection

There are 20 water quality monitoring sites in the Danjiangkou Reservoir Catchment. Four of these monitoring sites, Danjiangkou Dam, Taocha, Taizishan, and Langhekou, numbered R1, R2, R3, and R4, respectively (Fig. 1), and distributed near the Danjiangkou Dam, were used to measure the water quality in the reservoir. Another 16 of the monitoring sites, located near the mouths of the 16 tributaries, numbered S1 to S16 (Fig. 1), were used to measure the water quality in the 16 tributaries.

Water quality samples were collected monthly at four monitoring sites in the reservoir from 2005 to 2012, while samples were collected twice a month at 16 monitoring sites in the tributaries from January 2012 to December 2012. Seventeen water quality indices were selected for analysis. The analytical techniques for these indices can be found in the Chinese water quality analytical standards, such as *Determination of 34 Elements (Pb, Cd, V, P etc.)* (SL 394.1-2007), and the limit values of different water quality grades can be found

in the *Environmental Quality Standards for Surface Water* (GB 3838-2002). The range of observed values for each index is shown in Table 2, where DO, NH₃-N, TN, COD_{Mn}, BOD₅, CN⁻, Vola, TP, Surfa, and Coli are the abbreviations for dissolved oxygen, ammonia nitrogen, total nitrogen, permanganate index, five-day biochemical oxygen demand, cyanide, volatile phenol, total phosphorus, anionic surfactant, and fecal coliform.

3.2. Single factor evaluation method

Compared with the comprehensive index method, the single factor evaluation method is more conservative and considered to be more suitable for serious water pollution situations in China. In addition, the single factor evaluation method can expediently identify the primary water quality indices. Thus, the single factor evaluation method was used to calculate each water quality index. Through comparison of the calculated value of each index with the standard value, the grade for each index was determined. After the grades were determined for all 17 indices for each sample at each measuring site, the worst one was considered the grade for that site.

3.3. Seasonal Mann–Kendall test

The seasonal Mann–Kendall test is a kind of non-parametric test method, which can deal well with the missing values and seasonal changes in the data. It was put forward by Hirsch et al. (1982). It has been widely used in water quality trend testing and analysis (Bouza-Deaño et al., 2008; Yenilmez et al., 2011; Naddeo et al., 2013). The related equations for calculating the Mann–Kendall test statistic S and the standardized Mann–Kendall test statistic Z are as follows:

$$S = \sum_{i=1}^{12} S_i \quad (1)$$

$$S_i = \sum_{k=1}^{n-1} \sum_{j=k+1}^n \text{sgn}(X_{ij} - X_{ik}) \quad (2)$$

$$Z = \begin{cases} \frac{S-1}{\sqrt{\text{Var}(S)}} & S > 0 \\ 0 & S = 0 \\ \frac{S+1}{\sqrt{\text{Var}(S)}} & S < 0 \end{cases} \quad (3)$$

where X_{ij} is the water quality index of the i th month of the j th year, $\text{Var}(S)$ is the variance of S , and n is the number of years. Since the water quality condition is a random event, Z follows a standard normal distribution. Under no trend assumptions, Z is equal to zero. If Z is not equal to zero, the water quality index has an increasing trend ($Z > 0$) or a decreasing trend ($Z < 0$). Hirsch et al. (1982) suggested that the significance level be set as $\alpha = 0.1$ or $\alpha = 0.01$, indicating that the water

Table 1
Information for tributaries in study area.

| Tributary | Measuring site | Length (km) | Drainage area (km ²) | Mean discharge (m ³ /s) | Runoff (×10 ⁹ m ³) |
|----------------|----------------|-------------|----------------------------------|------------------------------------|---|
| Hanjiang River | S1 | 925 | 55,081 | 866.53 | 27.327 |
| Tianhe River | S2 | 84 | 1614 | 14.80 | 0.467 |
| Duhe River | S3 | 342 | 12,431 | 236.00 | 6.040 |
| Shending River | S4 | 58 | 227 | 1.52 | 0.048 |
| Jianghe River | S5 | 35 | 326 | 2.00 | 0.063 |
| Sihe River | S6 | 67 | 469 | 3.62 | 0.114 |
| Guanshan River | S7 | 67 | 465 | 7.78 | 0.245 |
| Jianhe River | S8 | 27 | 47 | 0.32 | 0.010 |
| Langhe River | S9 | 57 | 381 | 5.15 | 0.162 |
| Danjiang River | S10 | 384 | 7560 | 46.23 | 1.458 |
| Qihe River | S11 | 147 | 1598 | 12.10 | 0.382 |
| Taohe River | S12 | 155 | 1210 | 16.50 | 0.520 |
| Laoguan River | S13 | 254 | 4231 | 37.40 | 1.179 |
| Quyuan River | S14 | 53 | 312 | 1.74 | 0.055 |
| Jiangjun River | S15 | 23 | 62 | 0.44 | 0.014 |
| Taogou River | S16 | 27 | 45 | 0.30 | 0.011 |

Table 2
Ranges of water quality indices measured in Danjiangkou Reservoir and tributaries.

| Site | DO (mg/L) | NH ₃ -N (mg/L) | TN (mg/L) | COD _{Mn} (mg/L) | BOD ₅ (mg/L) | CN ⁻ (μg/L) | As (μg/L) | Vola (μg/L) | Cr ⁶⁺ (mg/L) | Hg (μg/L) | Cu (mg/L) | Cd (μg/L) | Pb (mg/L) | TP (mg/L) | Oil (mg/L) | Surfa (mg/L) | Coli (10 ⁴ ind./L) |
|------|-----------|---------------------------|-----------|--------------------------|-------------------------|------------------------|-----------|-------------|-------------------------|-----------|-------------|-----------|-----------|-----------|------------|--------------|-------------------------------|
| R1 | 4.8–11.7 | 0.060–0.241 | 0.9–1.0 | 1.0–3.3 | 0.3–2.3 | – | 0.2–10.8 | 2.0–7.0 | – | – | 0.005–0.018 | – | – | 0.01–0.05 | 0.01–0.03 | – | 0.002–0.014 |
| R2 | 5.2–13.4 | 0.060–0.500 | 0.7–2.0 | 0.8–3.0 | 0.3–2.4 | – | 0.2–14.7 | L | – | – | – | – | – | 0.01–0.04 | 0.01–0.06 | – | 0.01–0.18 |
| R3 | 5.1–11.5 | 0.050–0.280 | 1.0–2.13 | 0.8–2.8 | 0.3–2.6 | – | 0.2–12.3 | 2.0–7.0 | – | – | – | – | – | 0.01–0.05 | 0.01–0.04 | – | 0.002–0.019 |
| R4 | 4.8–11.8 | 0.060–0.239 | 0.7–1.6 | 1.0–3.5 | 0.3–2.6 | – | 0.2–10.8 | 2.0–3.0 | – | – | 0.005–0.018 | – | – | 0.01–0.06 | 0.01–0.04 | – | 0.002–0.017 |
| S1 | 7.2–13 | 0.045–0.449 | 1.11–2.31 | 1.0–3.2 | 0.3–3.2 | – | 0.7–2.0 | 0.3–2.8 | – | – | – | – | – | 0.02–0.15 | – | 0.05–0.08 | 0.075–16 |
| S2 | 7.0–13.3 | 0.061–2.320 | 0.62–5.81 | 1.3–2.6 | 0.5–5.1 | – | 1.1–2.1 | 0.4–4.0 | – | – | – | – | – | 0.04–0.26 | 0.02–0.04 | 0.05–0.15 | 0.11–16 |
| S3 | 4.7–12.3 | 0.051–1.205 | 0.70–2.85 | 1.3–3.4 | 0.5–3.7 | – | 0.7–1.6 | 0.3–2.8 | – | – | – | – | – | 0.01–0.35 | – | 0.05–0.08 | 0.025–8.17 |
| S4 | 0.7–5.3 | 5.450–14.80 | 10.5–40.8 | 5.2–18.1 | 3.5–136.1 | 4–15 | 0.8–2.4 | 0.9–10.5 | – | 0.01–0.43 | – | 9–52 | – | 0.52–2.67 | 0.01–1.22 | 0.05–0.77 | 1.7–160 |
| S5 | 1.6–11.8 | 0.743–8.700 | 2.17–10.1 | 2.4–20.9 | 1.8–22.7 | 4–13 | 1.1–4.6 | 0.3–9.5 | – | 0.01–0.09 | 0.005–0.006 | 8–12 | – | 0.08–2.46 | 0.01–0.07 | 0.05–0.27 | 1.7–160 |
| S6 | 1.6–11.8 | 2.110–8.480 | 4.60–15.6 | 3.4–7.6 | 2.1–11.3 | 4–31 | 1.3–4.2 | 0.3–4.9 | – | 0.01–0.08 | – | 1–28 | – | 0.28–0.99 | 0.02–0.05 | 0.05–0.37 | 1.7–160 |
| S7 | 5.6–13.4 | 0.070–1.220 | 0.49–3.88 | 2.1–5.6 | 0.6–2.8 | – | 0.8–3.4 | 0.6–4.6 | – | 0.01–0.07 | – | 1–14 | – | 0.04–0.52 | 0.01–0.04 | 0.05–0.12 | 0.02–92 |
| S8 | 2.2–18.0 | 0.100–16.40 | 0.95–18.5 | 3.2–11.5 | 0.5–5.8 | 5–36 | 1.0–2.8 | 0.4–3.6 | – | 0.01–0.07 | – | – | – | 0.03–0.44 | 0.01–0.06 | 0.05–0.25 | 0.02–16 |
| S9 | 7.0–19.6 | 0.072–1.200 | 0.58–4.08 | 1.8–5.9 | 0.6–4.3 | – | 0.9–0.95 | 0.4–6.5 | – | 0.01–2.27 | 0.005–0.015 | 1–11 | – | 0.02–0.66 | 0.01–0.05 | 0.05–0.47 | 0.02–9.2 |
| S10 | 7.2–13.7 | 0.033–1.435 | 1.51–7.88 | 1.1–3.8 | 0.7–3.3 | – | 1.1–3.3 | 0.4–6.8 | – | 0.01–0.05 | – | – | – | 0.01–0.24 | – | 0.05–0.11 | 0.02–1.4 |
| S11 | 7.0–15.4 | 0.032–0.533 | 0.65–3.81 | 1.0–3.5 | 0.5–2.0 | – | 0.9–3.3 | 0.4–1.9 | – | 0.01–0.05 | – | – | – | 0.01–0.17 | 0.01–0.04 | 0.05–0.08 | 0.02–1.1 |
| S12 | 7.6–14.9 | 0.025–0.176 | 0.41–2.15 | 0.9–2.6 | 0.5–2.0 | – | 0.8–3.0 | 0.3–3.7 | – | – | – | 1–19 | – | 0.01–0.04 | 0.01–0.02 | 0.05–0.08 | 0.02–0.49 |
| S13 | 5.6–18.5 | 0.159–2.840 | 2.25–11.0 | 1.9–5.2 | 0.6–8.0 | 4–6 | 0.5–5.7 | 0.3–2.0 | – | 0.01–1.5 | – | 1–8 | – | 0.04–0.14 | – | 0.05–2.10 | 0.2–54 |
| S14 | 4.5–13.4 | 0.032–0.846 | 0.40–2.87 | 0.8–2.4 | 0.4–3.7 | – | 0.9–2.2 | 0.3–2.5 | – | – | – | – | – | 0.02–0.13 | 0.01–0.03 | 0.05–0.09 | 0.02–16 |
| S15 | 7.9–13.1 | 0.028–0.310 | 0.91–2.76 | 0.9–3.2 | 0.4–2.2 | – | 0.5–1.8 | 0.3–3.4 | – | – | – | – | – | 0.01–0.08 | 0.01–0.04 | 0.05–0.09 | 0.02–9.2 |
| S16 | 8.4–18.9 | 0.049–0.189 | 0.14–4.68 | 0.6–4.8 | 0.5–2.2 | – | 0.6–2.4 | 0.3–6.8 | – | 0.01–0.05 | – | – | – | 0.01–0.08 | – | 0.05–0.44 | 0.02–9.2 |

quality index has a significant trend or a highly significant trend, respectively. According to the standard normal distribution function, the absolute value of Z is 1.645 when $\alpha = 0.1$ and 2.575 when $\alpha = 0.01$. That is to say, if the calculated value of Z is greater than 2.575, the water quality index has a highly significant increasing trend; if $1.645 < Z < 2.575$, the water quality index has a significant increasing trend; if $0 < Z < 1.645$, the water quality index has no significant increasing trend; if $Z < -2.575$, the water quality index has a highly significant decreasing trend; if $-2.575 < Z < -1.645$, the water quality index has a significant decreasing trend; and if $-1.645 < Z < 0$, the water quality index has no significant decreasing trend (Xin et al., 2012).

3.4. Two-dimensional water quality numerical model

The two-dimensional water quality numerical model MIKE 21 AD (DHI, 2001) is suitable for simulating and predicting the water quality index distributions for rivers, lakes, and reservoirs, and it has been widely used in this field (Lindim et al., 2011; Zhou et al., 2011; Sokolova et al., 2013; Zhang and Xin, 2013). Thus, it was used to compute the water quality index distributions in the Danjiangkou Reservoir by solving the shallow water equations and the convection–diffusion equation. The model was validated in the flood season (July) and the dry season (December) using a Manning roughness value of 0.03 and degradation coefficients of 0.04 d^{-1} and 0.0004 d^{-1} for COD_{Mn} and TP, respectively. The validation results are listed in Table 3, where V_f is the measured value, V_s is the simulated value, and E_r is the relative error. As shown in Table 3, the range of error is between -10.0% and 10.0% , which is an acceptable level of agreement.

4. Results and discussion

4.1. Water quality status and primary water quality indices

4.1.1. Water quality status of Danjiangkou Reservoir

There are 12 samples for the four measuring sites in the Danjiangkou Reservoir in 2012. The results for four main water quality indices (TP, COD_{Mn} , DO, and BOD_5) are listed in Table 4, and the remaining water quality indices are all below the threshold of Grade I. This indicates that the water quality in the reservoir is quite good, and can satisfy the goal in almost every month at each site. Thus, the four main indices are the control indicators for determination of the water quality grade of the Danjiangkou Reservoir.

The box plots of the main water quality indices are shown in Fig. 2. As shown in Fig. 2, the mean values of TP concentration are equal to or less than 0.02 mg/L at the four measuring sites (the upper limit of Grade II for the lake or reservoir is 0.025 mg/L), and the mean values of DO concentration are greater than 8.0 mg/L at the four sites (the lower limit of Grade I is 7.5 mg/L). The mean values of COD_{Mn} and BOD_5 concentrations are less than 2.5 mg/L and 1.5 mg/L , respectively, both of which are less than the upper limit of Grade II.

Table 3
Comparison between simulated and observed water quality indices.

| Site | COD _{Mn} | | | | | | TP | | | | | |
|------|-----------------------|-----------------------|---------------------|-----------------------|-----------------------|---------------------|-----------------------|-----------------------|---------------------|-----------------------|-----------------------|---------------------|
| | Flood season | | | Dry season | | | Flood season | | | Dry season | | |
| | V _f (mg/L) | V _s (mg/L) | E _{rr} (%) | V _f (mg/L) | V _s (mg/L) | E _{rr} (%) | V _f (mg/L) | V _s (mg/L) | E _{rr} (%) | V _f (mg/L) | V _s (mg/L) | E _{rr} (%) |
| R1 | 2.0 | 2.1 | 5.0 | 2.1 | 2.0 | −4.8 | 0.02 | 0.02 | 0 | 0.02 | 0.018 | −10.0 |
| R2 | 2.4 | 2.2 | −8.3 | 2.2 | 2.0 | −9.1 | 0.02 | 0.02 | 0 | 0.02 | 0.018 | −10.0 |
| R3 | 2.1 | 2.2 | 4.8 | 2.0 | 2.0 | 0 | 0.02 | 0.02 | 0 | 0.02 | 0.018 | −10.0 |
| R4 | 2.0 | 2.2 | 10.0 | 2.0 | 2.2 | 10.0 | 0.02 | 0.02 | 0 | 0.02 | 0.020 | 0 |

Table 4
Percentages of different grades of water quality and main water quality indices in Danjiangkou Reservoir.

| Site | Percentage of grade of water quality (%) | | | | | | Goal grade | Main water quality index |
|------|--|------|-----|----|---|---------------|------------|--|
| | I | II | III | IV | V | Inferior to V | | |
| R1 | 0 | 100 | 0 | 0 | 0 | 0 | II | TP, COD _{Mn} , DO |
| R2 | 0 | 91.7 | 8.3 | 0 | 0 | 0 | | TP, COD _{Mn} , BOD ₅ |
| R3 | 0 | 100 | 0 | 0 | 0 | 0 | | TP, COD _{Mn} , DO |
| R4 | 0 | 91.7 | 8.3 | 0 | 0 | 0 | | TP, COD _{Mn} , BOD ₅ |

4.1.2. Water quality status of tributaries

There are 24 samples from the tributaries in 2012. Table 5 shows that the grades for TP, BOD₅, NH₃–N, COD_{Mn}, DO, and Surfa exceed the goal grades for tributaries, The water quality in the Hanjiang (S1), Qihe (S11), Taohe (S12), and Jiangjun (S15) rivers is relatively good, while the water quality in the Shending (S4), Jianghe (S5), Sihe (S6), Guanshan (S7), Jianhe (S8), and Langhe (S9) rivers is poor. The box plots of the water quality indices exceeding the standard levels are shown in Fig. 3. It can be seen from Fig. 3 that the mean values of the indices are relatively high at sites 4, 5, 6 and 8.

Table 5
Percentages of different grades of water quality and water quality indices exceeding standards in tributaries.

| Site | Percentage of grade of water quality (%) | | | | | | Goal | Standard-exceeding grade index |
|------|--|------|------|------|------|---------------|------|--|
| | I | II | III | IV | V | Inferior to V | | |
| S1 | 16.7 | 70.8 | 12.5 | 0 | 0 | 0 | II | BOD ₅ |
| S2 | 0 | 50.0 | 29.1 | 16.7 | 0 | 4.2 | III | TP, NH ₃ –N, BOD ₅ |
| S3 | 29.2 | 25.0 | 20.8 | 16.7 | 8.3 | 0 | II | TP, NH ₃ –N, DO |
| S4 | 0 | 0 | 0 | 0 | 0 | 100 | IV | TP, NH ₃ –N, DO, COD _{Mn} , BOD ₅ , Surfa |
| S5 | 0 | 0 | 0 | 12.5 | 20.8 | 66.7 | IV | TP, NH ₃ –N, COD _{Mn} , BOD ₅ |
| S6 | 0 | 0 | 0 | 0 | 0 | 100 | III | TP, NH ₃ –N, DO, COD _{Mn} , BOD ₅ , Surfa |
| S7 | 0 | 20.8 | 50.0 | 20.8 | 4.2 | 4.2 | II | TP, NH ₃ –N, COD _{Mn} |
| S8 | 0 | 4.2 | 25.0 | 29.2 | 8.3 | 33.3 | II | TP, NH ₃ –N, DO, COD _{Mn} , BOD ₅ |
| S9 | 4.2 | 29.2 | 8.3 | 29.2 | 8.3 | 20.8 | II | TP, NH ₃ –N, COD _{Mn} , BOD ₅ , Surfa |
| S10 | 12.5 | 33.3 | 37.5 | 16.7 | 0 | 0 | II | TP, NH ₃ –N |
| S11 | 45.9 | 33.3 | 20.8 | 0 | 0 | 0 | II | NH ₃ –N |
| S12 | 66.7 | 25.0 | 8.3 | 0 | 0 | 0 | II | NH ₃ –N, COD _{Mn} , BOD ₅ |
| S13 | 0 | 41.6 | 20.8 | 16.7 | 16.7 | 4.2 | III | DO |
| S14 | 4.2 | 62.4 | 16.7 | 16.7 | 0 | 0 | II | NH ₃ –N, Surfa |
| S15 | 50.0 | 33.3 | 16.7 | 0 | 0 | 0 | II | NH ₃ –N |
| S16 | 41.6 | 29.2 | 20.8 | 4.2 | 0 | 4.2 | III | Surfa |

4.2. Temporal trends of primary indices

Based on monthly monitoring data from the four measuring sites in the Danjiangkou Reservoir from 2005 to 2012, calculated values of Z are listed in Table 6. The concentrations of BOD₅ at the four sites are lower than the detection limit from 2005 to 2009, so trend analysis is unavailable. As can be seen in Table 6, at all four sites, the values of Z for COD_{Mn} are greater than 2.575, indicating that the COD_{Mn} concentration shows a highly significant increasing trend. This results from increasing loads from the tributaries, particularly the Shending, Sihe, Guanshan, Jianhe, and Langhe rivers. These rivers run through counties and towns where serious pollution exists and the pollution load is from domestic sewage and agricultural runoff. At the Danjiangkou Dam (R1) and Taocha (R2) sites, the values of Z for TP are greater than 1.645, which implies that the TP concentration has a significant increasing trend. Agricultural runoff is one of the most important sources of TP, especially in the upper reaches of the Hanjiang and Duhe rivers, where there are irrigated areas and mountain

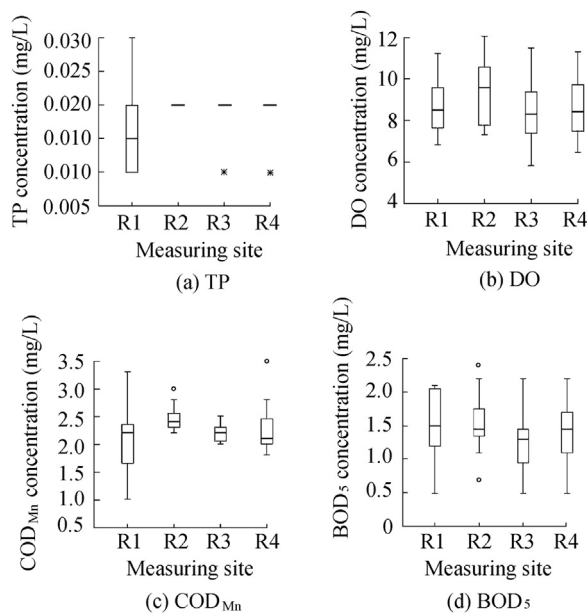


Fig. 2. Box plots of main water quality indices in Danjiangkou Reservoir (° denotes the outlier that lies outside the range of 1.5 times the interquartile, and * denotes the outlier that lies outside the range of three times the interquartile).

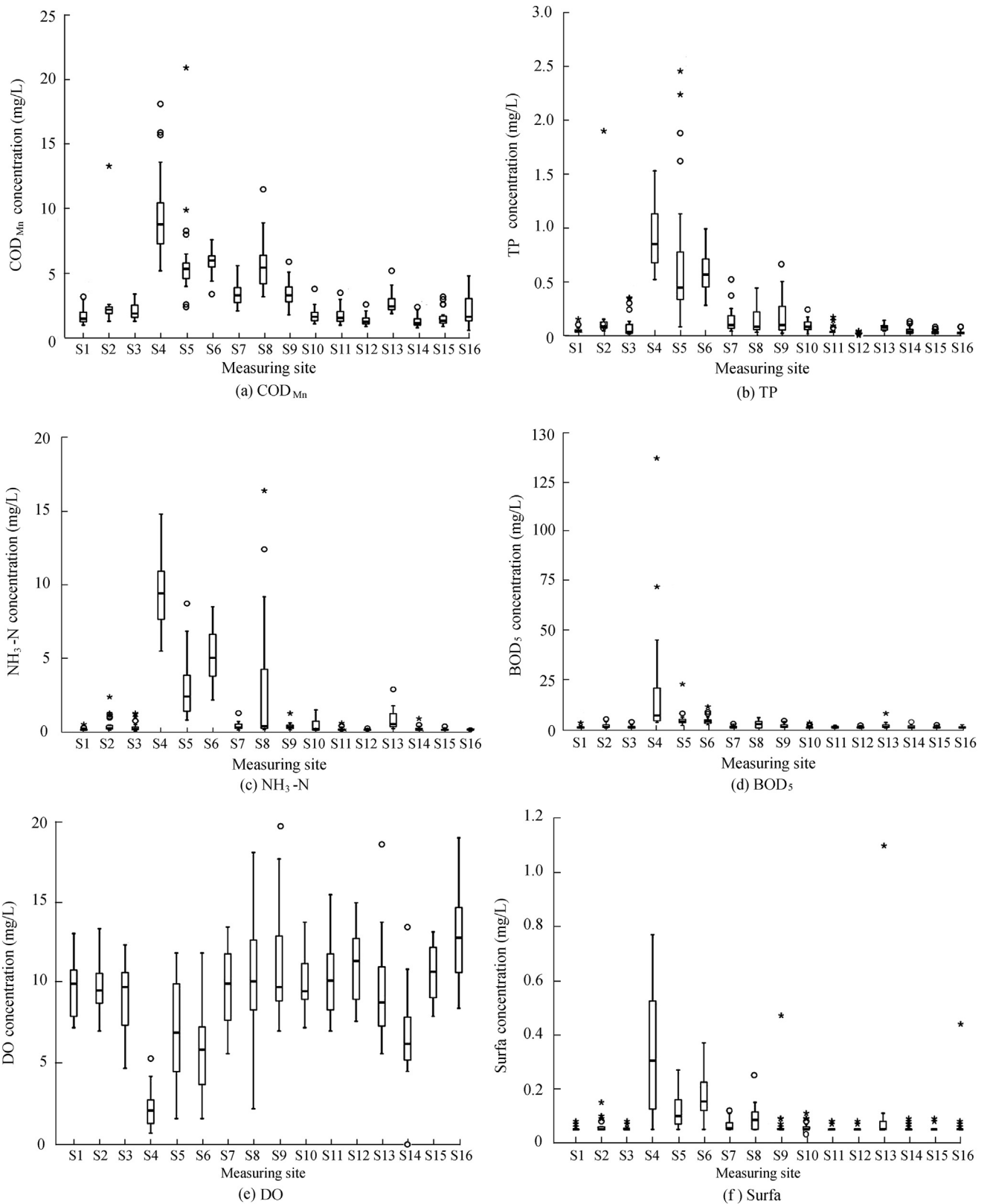


Fig. 3. Box plots of water quality indices exceeding standard levels in tributaries (° denotes the outlier that lies outside the range of 1.5 times the interquartile, and * denotes the outlier that lies outside the range of three times the interquartile).

Table 6
Values of Z for different water quality indices at four measuring sites.

| Site | Z | | |
|------|-------------------|--------|--------|
| | COD _{Mn} | DO | TP |
| R1 | 4.176 | 1.036 | 1.771 |
| R2 | 3.508 | −1.652 | 1.652 |
| R3 | 4.042 | −0.434 | −0.702 |
| R4 | 3.775 | −0.234 | −0.234 |

farmlands. At the Taocha site (R2), the Z value for DO is less than −1.645, indicating that the DO concentration has a significant decreasing trend, which implies that the organic pollutants that consume oxygen are increasing.

4.3. Prediction of concentration distributions

Point and non-point sources in the 16 main tributaries are the main contributors of pollutants to the Danjiangkou Reservoir. Runoff in the Hanjiang Basin is concentrated in the

flood season ($\geq 75\%$), but the stored water volume in the Danjiangkou Dam is kept low to provide the flood mitigation. Therefore, water quality is worse in the flood season than in the dry season. The distributions of TP and COD_{Mn} concentrations in two cases were predicted using the MIKE 21 AD model. The first case assumes that the TP and COD_{Mn} concentrations in 16 tributaries reach their highest measured values synchronously, and the second case assumes that the TP and COD_{Mn} concentrations of 16 tributaries reach the upper limits of their goal grades. Fig. 4 shows the distributions of the predicted TP concentration in the two cases, and Fig. 5 shows the distributions of the predicted COD_{Mn} concentration in the two cases.

As can be seen in Table 6, the TP concentration in the Danjiangkou Reservoir shows a significantly increasing trend, especially at the Danjiangkou Dam and Taocha sites, and this is unfavorable to the SNWDP. Fig. 4(a) implies that if the TP concentrations in the tributaries are not controlled, especially in the Hanjiang and Duhe rivers, which have the largest and second largest discharges, the water quality in almost half the

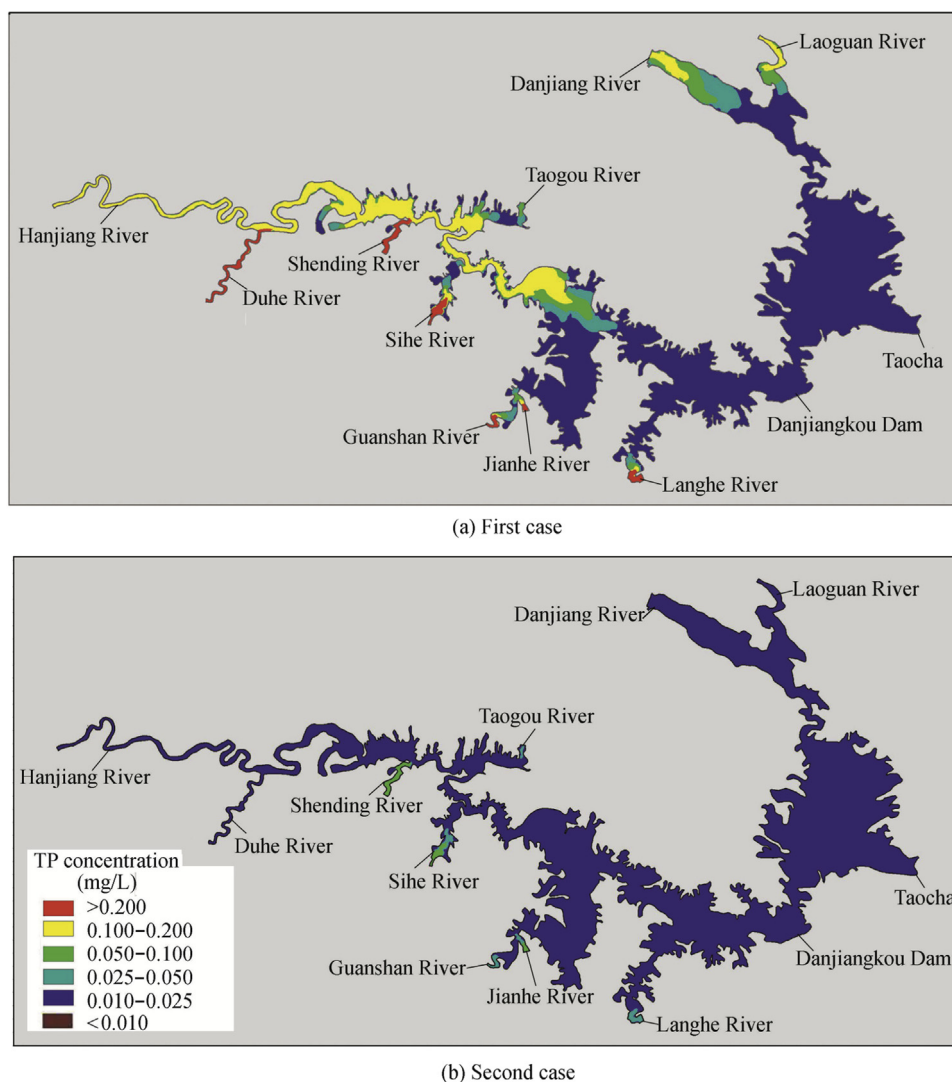


Fig. 4. Distributions of predicted TP concentration in Danjiangkou Reservoir and tributaries in two cases.

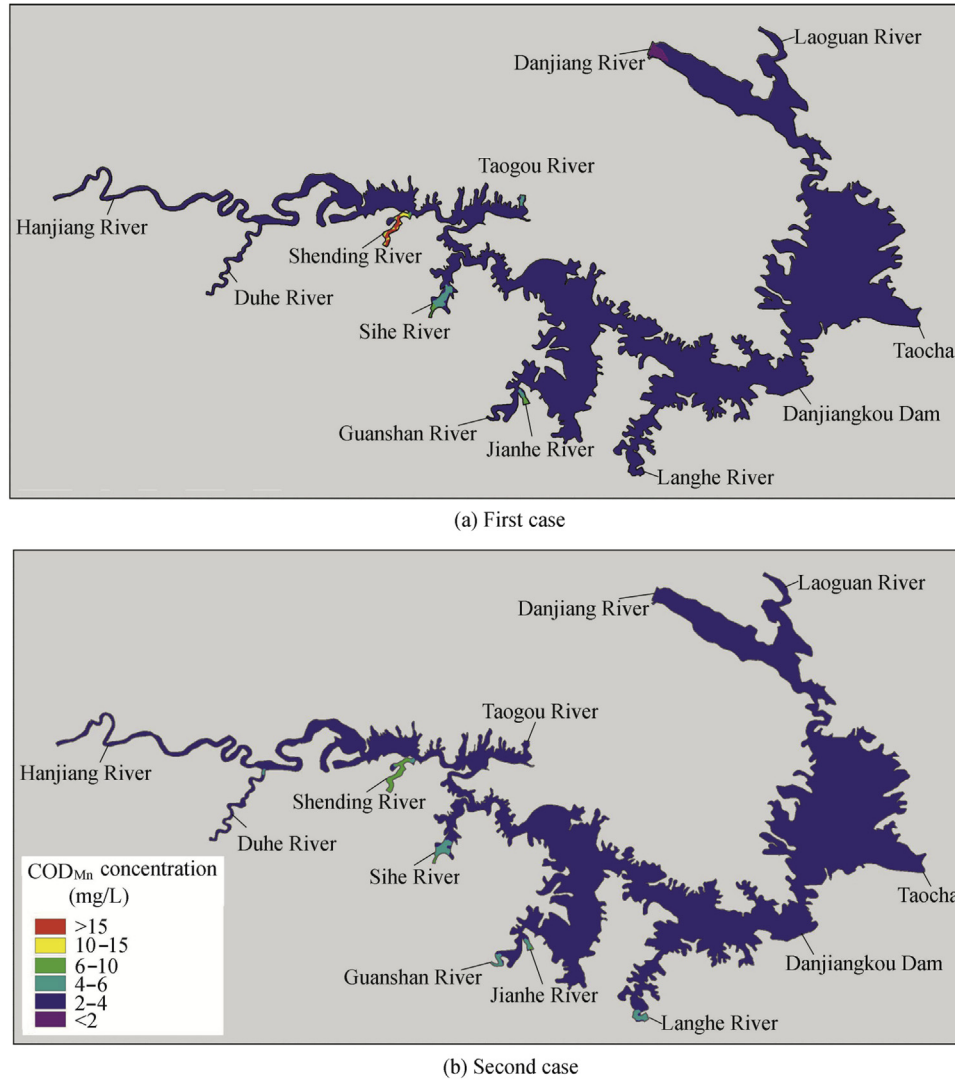


Fig. 5. Distributions of predicted COD_{Mn} concentration in Danjiangkou Reservoir and tributaries in two cases.

area of the Han Reservoir will not meet the required goal, since the current concentration of TP is close to the upper limit for Grade II. Thus, control of TP concentration will be the focus of water pollution management in this zone.

Fig. 5(a) shows that, although the water quality in the tributaries does not meet the goal, the COD_{Mn} pollution plumes remain restricted to the tributaries, because the background concentration of COD_{Mn} in the Danjiangkou Reservoir is low and the discharges of the tributaries are relatively small. However, the increasing trend of COD_{Mn} concentration at the four measuring sites in the reservoir implies that there exists a potential threat to water quality in the Danjiangkou Reservoir. Fig. 5(b) shows that, even if water quality in the tributaries satisfies their goals, improvement of the water quality in the tributaries is still necessary in order to ensure that the water quality in the reservoir reaches its goal, because there are different water quality goal requirements for the tributaries (Grade IV, III or II) and the Danjiangkou Reservoir (Grade II).

4.4. Water quality protection strategy

4.4.1. Tributary classification

Tributaries are the key points for water quality protection in the Danjiangkou Reservoir, and the question arises as to which tributaries' water quality should be improved first. We approach this problem by classifying the 16 main tributaries using a hierarchical clustering method. Based on six main water quality indices, TP, BOD_5 , $\text{NH}_3\text{-N}$, COD_{Mn} , DO, and Surfa, a dendrogram of tributaries made using Ward's method is shown in Fig. 6, where D_{link} is the linkage distance, and D_{max} is the maximum linkage distance. As can be seen in Fig. 6, the 16 tributaries fall into three distinct clusters: the light-pollution cluster (cluster 1), moderate-pollution cluster (cluster 2), and heavy-pollution cluster (cluster 3). Cluster 1 consists of the Qihe, Jiangjun, Hanjiang, Taohe, Tianhe, Danjiang, Duhe, Laoguan, Qu Yuan, Guanshan, Langhe, and Taogou rivers. Cluster 2 consists of the Jianghe, Sihe, and Jianhe rivers, and cluster 3 is formed by the Shending River.

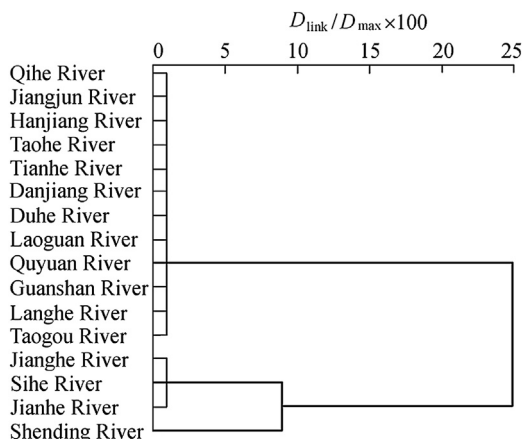


Fig. 6. Dendrogram of tributaries made using Ward's method based on six main water quality indices.

This implies that the Shending River is heavily polluted, because this tributary runs though the Maojian and Zhanwan counties and receives a lot of domestic and industrial sewage.

4.4.2. Seasonal classification

The pollution load from pollution sources may vary seasonally, especially for non-point source pollution. Thus, identification of the primary pollution period is equally important. Hierarchical clustering was also used to classify the months using the COD_{Mn} concentrations at the Danjiangkou Dam site. Three clusters can be seen in Fig. 7. March, April, and November cluster together as light-pollution months; January, December, and February are moderate-pollution months; and the remaining months (May to October), which constitute the wet season, have heavy pollution. Thus, we can infer that non-point source pollution is the primary pollution source in the Danjiangkou Reservoir zone.

4.4.3. Water protection strategy

Since industrial point sources have been removed, and the heavy metal, oil, and other inorganic contaminants are not the principal pollutants in the Danjiangkou Reservoir area, attention should be paid to domestic pollution and agricultural non-point source pollution. Considering the characteristics of

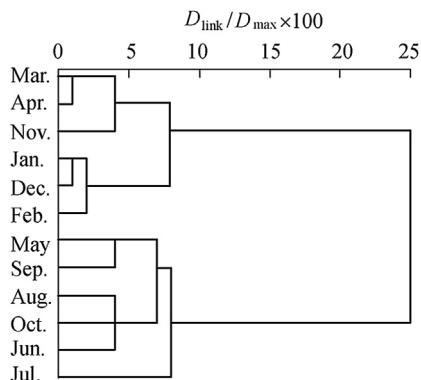


Fig. 7. Dendrogram of months made using Ward's method based on COD_{Mn} concentrations.

these two sources, water quality remediation should treat each tributary basin as a single unit.

The water protection strategy is as follows:

It is first necessary to determine the water environmental capacity of the Danjiangkou Reservoir and the tributaries. Based on this, it is possible to determine allowable pollutant loads that can be discharged into the tributaries. The allowable pollutant loads should be allocated among the industrial point sources, domestic point sources, and non-point sources.

Second, emergency measures should be taken to control the pollutant load of the Shending Basin. Sewage pipelines should be constructed to deliver sewage to treatment plants. Industrial plants should be required to treat their effluent on-site prior to discharging it.

Third, priority should be given to the construction of township sewage treatment plants and pipelines in the Shending, Jianghe, Sihe, and Jianhe basins. Vegetation projects should be arranged in the upper reaches of the Hanjiang and Duhe rivers.

Finally, there should be planning for water pollution control for all the 16 main tributaries and the other small tributaries, based on their water environmental capacity, and the pollution sources should be monitored to ensure that the load reduction is achieved.

5. Conclusions

Integrated research on the evaluation, prediction, and protection of the Danjiangkou Reservoir was carried out in this study. The following conclusions can be drawn:

(1) The overall water quality in the Danjiangkou Reservoir is quite good, as it meets the water quality requirement of the SNWDP (Grade II), and most of the water quality indices can reach the Grade I standard. The water quality in the 16 main tributaries is relatively poor, especially that of the Shending, Jianghe, Sihe, and Jianhe rivers. The main water quality indices that exceed the standard in these tributaries are TP, BOD_5 , NH_3-N , COD_{Mn} , DO, and Surfa, which is a serious threat to the water quality in the Danjiangkou Reservoir.

(2) Of the main water quality indices in the Danjiangkou Reservoir, the COD_{Mn} concentration shows a highly significant increasing trend, and the TP concentration shows a significant increasing trend. COD_{Mn} originates mainly from domestic and industrial point sources in the tributary basins, and TP comes mainly from agricultural non-point sources.

(3) Predictions of the distributions of main water quality indices imply that, without remediation measures, the water quality in half the area of the Han Reservoir will fail to meet the required standard, endangering the quality of the source water for the SNWDP.

(4) Tributary classification results implied that the 16 tributaries can be divided into three clusters; the Shending River is heavily polluted; the Jianghe, Sihe, and Jianhe rivers are moderately polluted; and they should be the focus of environmental remediation. According to the pollution degree, some management, planning, and engineering measures should be taken to control the pollution loads from the tributary basins.

(5) Long-term water quality monitoring in the Danjiangkou Reservoir area should be carried out to illustrate the water quality change trends. Water quality restoration technologies should be further researched.

References

- Bao, L.J., Maruya, K.A., Snyder, S.A., Zeng, E.Y., 2012. China's water pollution by persistent organic pollutants. *Environ. Pollut.* 163, 100–108. <http://dx.doi.org/10.1016/j.envpol.2011.12.022>.
- Booker, D.J., Woods, R.A., 2014. Comparing and combining physically-based and empirically-based approaches for establishing the hydrology of ungauged catchments. *J. Hydrol.* 508, 227–239. <http://dx.doi.org/10.1016/j.jhydrol.2013.11.007>.
- Bouza-Deaño, R., Ternero-Rodríguez, M., Fernández-Espinosa, A.J., 2008. Trend study and assessment of surface water quality in the Ebro River (Spain). *J. Hydrol.* 361 (3–4), 227–239. <http://dx.doi.org/10.1016/j.jhydrol.2008.07.048>.
- Chang, H., 2008. Spatial analysis of water quality trends in the Han River basin, South Korea. *Water Res.* 42 (13), 3285–3304. <http://dx.doi.org/10.1016/j.watres.2008.04.006>.
- Crosa, G., Froebrich, J., Nikolayenko, V., Stefani, F., Galli, P., Calamari, D., 2006. Spatial and seasonal variations in the water quality of the Amu Darya River (Central Asia). *Water Res.* 40 (11), 2237–2245. <http://dx.doi.org/10.1016/j.watres.2006.04.004>.
- Danish Hydraulic Institute (DHI), 2001. MIKE 21 User Guide and Reference Manual. DHI, Horsholm.
- El-Shaarawi, A.H., Esterby, S.R., Kuntz, K.W., 1983. A statistical evaluation of trends in the water quality of the Niagara River. *J. Gt. Lakes Res.* 9 (2), 234–240. [http://dx.doi.org/10.1016/S0380-1330\(83\)71892-7](http://dx.doi.org/10.1016/S0380-1330(83)71892-7).
- Gevrey, M., Comte, L., de Zwart, D., Lek, S., 2010. Modeling the chemical and toxic water status of the Scheldt basin (Belgium), using aquatic invertebrate assemblages and an advanced modeling method. *Environ. Pollut.* 158 (10), 3209–3218. <http://dx.doi.org/10.1016/j.envpol.2010.07.006>.
- Hirsch, R.M., Slack, J.R., Smith, R.A., 1982. Nonparametric test for trend in water quality. *Water Resour. Res.* 18, 107–121. <http://dx.doi.org/10.1029/WR020i001p00127>.
- Hu, Y.N., Cheng, H.F., 2013. Water pollution during China's industrial transition. *Environ. Dev.* 8, 57–73. <http://dx.doi.org/10.1016/j.envdev.2013.06.001>.
- Kundzewicz, Z.W., Robson, A.J., 2004. Change detection in hydrological records: a review of the methodology. *Hydrol. Sci. J.* 49 (1), 7–19.
- Lindim, C., Pinho, J.L., Vieira, J.M.P., 2011. Analysis of spatial and temporal patterns in a large reservoir using water quality and hydrodynamic modeling. *Ecol. Model.* 222 (14), 2485–2494. <http://dx.doi.org/10.1016/j.ecolmodel.2010.07.019>.
- Long, J., Ji, H.F., Huang, Z.Y., 2009. Application of time series analysis in water quality prediction. *Chin. J. Sci. Instrum.* 30 (6), 350–352 (in Chinese).
- Naddeo, V., Scannapieco, D., Zarra, T., Belgiorio, V., 2013. River water quality assessment: implementation of non-parametric tests for sampling frequency optimization. *Land Use Policy* 30 (1), 197–205. <http://dx.doi.org/10.1016/j.landusepol.2012.03.013>.
- Nasiri, F., Maqsood, I., Huang, G., Fuller, N., 2007. Water quality index: a fuzzy river-pollution decision support expert system. *J. Water Resour. Plan. Manag.* 133 (2), 95–105. [http://dx.doi.org/10.1061/\(ASCE\)0733-9496\(2007\)133:2\(95\)](http://dx.doi.org/10.1061/(ASCE)0733-9496(2007)133:2(95)).
- Nives, S.G., 1999. Water quality evaluation by index in Dalmatia. *Water Res.* 33 (16), 3423–3440. [http://dx.doi.org/10.1016/S0043-1354\(99\)00063-9](http://dx.doi.org/10.1016/S0043-1354(99)00063-9).
- Olsen, R.L., Chappell, R.W., Loftis, J.C., 2012. Water quality sample collection, data treatment and results presentation for principal components analysis: literature review and Illinois River watershed case study. *Water Res.* 46 (9), 3110–3112. <http://dx.doi.org/10.1016/j.watres.2012.03.028>.
- Ott, W.R., 1978. *Water Quality Indices: a Survey of Indices Used in the United States*. US Environmental Protection Agency, Washington, D.C.
- Paul, M.J., Meyer, J.L., 2001. Streams in the urban landscape. *Annu. Rev. Ecol. Syst.* 32, 333–365. <http://dx.doi.org/10.1146/annurev.ecolsys.32.081501.114040>.
- Seeboonruang, U., 2012. A statistical assessment of the impact of land uses on surface water quality indexes. *J. Environ. Manag.* 101, 134–142. <http://dx.doi.org/10.1016/j.jenvman.2011.10.019>.
- Simeonov, V., Stratis, J.A., Samara, C., Zachariadis, G., Voutsas, D., Anthemidis, A., Sofoniou, M., Kouimtzis, T., 2003. Assessment of the surface water quality in Northern Greece. *Water Res.* 37 (17), 4119–4124. [http://dx.doi.org/10.1016/S0043-1354\(03\)00398-1](http://dx.doi.org/10.1016/S0043-1354(03)00398-1).
- Sokolova, E., Pettersson, T.J.R., Bergstedt, O., Hermansson, M., 2013. Hydrodynamic modeling of the microbial water quality in a drinking water source as input for risk reduction management. *J. Hydrol.* 497, 15–23. <http://dx.doi.org/10.1016/j.jhydrol.2013.05.044>.
- Vanlandeghem, M.M., Meyer, M.D., Cox, S.B., Sharma, B., Patiño, R., 2012. Spatial and temporal patterns of surface water quality and ichthyotoxicity in urban and rural river basins in Texas. *Water Res.* 46 (20), 6638–6651. <http://dx.doi.org/10.1016/j.watres.2012.05.002>.
- Xin, X.K., Yin, W., Yang, F., 2012. Research on water quality evolution trend of Danjiangkou Reservoir by Kendall Method. *Yangtze River* 43 (13), 91–94 (in Chinese).
- Xu, H.S., Xu, Z.X., Wu, W., Tang, F.F., 2012. Assessment and spatiotemporal variation analysis of water quality in the Zhangweinan River Basin, China. *Procedia Environ. Sci.* 13, 1641–1652. <http://dx.doi.org/10.1016/j.proenv.2012.01.157>.
- Xu, Z.X., 2005. Single factor water quality identification index for environmental quality assessment of surface water. *J. Tongji Univ. (Nat. Sci.)* 33 (3), 321–325 (in Chinese).
- Yenilmez, F., Keskin, F., Aksoya, A., 2011. Water quality trend analysis in Eymir Lake, Ankara. *Phys. Chem. Earth Parts A/B/C* 36 (5–6), 135–140. <http://dx.doi.org/10.1016/j.pce.2010.05.005>.
- Zhang, S.P., Xin, X.K., 2013. Application of MIKE 21 Module in waste drainage outlet arrangement for enterprise sewage treatment plant. *Water Resour. Power* 31 (9), 101–104 (in Chinese).
- Zhao, Y., Xia, X.H., Yang, Z.F., Wang, F., 2012. Assessment of water quality in Baiyangdian Lake using multivariate statistical techniques. *Procedia Environ. Sci.* 13, 1213–1226. <http://dx.doi.org/10.1016/j.proenv.2012.01.115>.
- Zhou, N.Q., Westrich, B., Jiang, S.M., Wang, Y., 2011. A coupling simulation based on a hydrodynamics and water quality model of the Pearl River Delta, China. *J. Hydrol.* 396 (3–4), 267–276. <http://dx.doi.org/10.1016/j.jhydrol.2010.11.019>.
- Zhu, D.S., Zhang, J.Y., Shi, X.X., Yin, W., 2011. Modern water resources protection planning technology system. *Water Resour. Prot.* 27 (5), 28–31 (in Chinese).